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(71) Applicant (<i>for all designated States except US</i>): COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; 407 Royal Parade, Parkville, VIC 3052 (AU).			
(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): HUGHES, Anthony, Ewart [AU/AU]; Fayre Lodge, 78 Olinda-Monbulk Road, Olinda, VIC 3788 (AU). TURNEY, Terence, William [AU/AU]; 47 Surrey Road, Mount Waverley, VIC 3149 (AU). NELSON, Karen, Joy, Hammon [AU/AU]; 2/12 Renver Road, Clayton, VIC 3168 (AU).			
(74) Agent: PHILLIPS ORMONDE & FITZPATRICK; 367 Collins Street, Melbourne, VIC 3000 (AU).			

(54) Title: PROCESS AND SOLUTION FOR PROVIDING A CONVERSION COATING ON A METAL SURFACE

(57) Abstract

A process and an aqueous, acidic solution for forming a rare earth element containing coating on the surface of a metal, said solution including effective quantities of: (a) one or more rare earth element containing species including at least one rare earth element capable of having more than one higher valence state, as herein defined; and (b) one or more additives selected from the groups including: i) aqueous metal complexes including at least one peroxy ligand; and ii) metal salts or aqueous metal complexes of a conjugate base of an acid in which the metals are selected from Transition Elements and Group IVA elements of the Periodic Table as herein defined.

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PROCESS AND SOLUTION FOR PROVIDING A CONVERSION COATING ON A METAL SURFACE

FIELD OF THE INVENTION

5 This invention relates to a process for forming a conversion coating on metal surfaces and a solution for use in said process. The invention extends to the conversion coated metal thus formed. The invention is particularly concerned with a process and solution for forming a conversion coating on aluminium or aluminium alloy, and the conversion coated aluminium or aluminium thus formed.

10

BACKGROUND OF THE INVENTION

The term "conversion coating" is a well known term of the art and refers to the replacement of native oxide on the surface of a metal by the controlled chemical formation of a film. Oxides or phosphates are common conversion coatings.
15 Conversion coatings are used on metals such as aluminium, iron, zinc, cadmium or magnesium and their alloys, and provide a key for paint adhesion and/or corrosion protection of the substrate metal. Accordingly, conversion coatings find application in such areas as the aerospace, architectural and building industries.

Known methods for applying conversion coatings to metal surfaces
20 include treatment with chromate or phosphate solutions, or mixtures thereof. However, in recent years it has been recognised that the hexavalent chromium ion, Cr⁶⁺, is a serious environmental and health hazard. Phosphate ions can also be detrimental, particularly when they find their way into natural waterways and cause algal blooms. Consequently, strict restrictions have been placed on industrial
25 processes and limitations have been placed on the release of such solutions to the environment. This leads to costly effluent processing.

In the search for alternative, less toxic conversion coatings, research has been conducted on conversion coatings based on rare earth compounds. One prior conversion coating process has been described in Australian patent specification
30 AU-A-14858/88 which is incorporated herein by reference. That conversion coating process comprises contacting a metal surface with a solution formed by an aqueous

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acidic solution containing cerium and H₂O₂ in which some or all of the cerium has been oxidised to the +4 valence state. It is asserted in AU-A-14858/88 that an increase in the solution pH in the region of the metal surface to a sufficiently high value causes precipitation of a cerium containing coating on the metal surface.

5 There is, however, considerable room for improvement in the properties of
prior rare earth element based conversion coatings, such as adhesion, and in the
time required to deposit those coatings. The need for improvement is particularly
true for conversion coatings on certain metal alloys, such as 3000, 5000 and 6000
series aluminium alloys, which coatings can be slow to deposit and have variable
10 adherence or no adherence.

Accordingly, it is an object of the present invention to provide a process and solution for forming a conversion coating on a metal surface which overcome, or at least alleviate, one or more of the disadvantages or deficiencies of the prior art. It is also an object of the present invention to provide conversion coated metal surface formed by the process of the invention.

It has been discovered that addition of one or more additives, having particular compositions, to the coating solution can assist in accelerating the coating process and/or improving adhesion of the conversion coating to the metal surface.

Throughout the specification, reference will be to the CAS version of the
20 Periodic Table, as defined in (for example) Chemical and Engineering News, 63(5),
27, 1985. Furthermore, as used herein, the term "transition elements" or "transition
metals" refers to the elements of the Periodic Table from scandium to zinc
inclusively, yttrium to cadmium inclusively and lanthanum to mercury inclusively.
Moreover, as used herein, the term "rare earth" elements, metals or cations refer to
25 the elements of the Lanthanide series, namely those having the atomic number 57
to 71 (La to Lu), plus scandium and yttrium. In addition, the term "higher valence
state" means a valence state above zero valency.

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SUMMARY OF THE INVENTION

According to the present invention, there is provided an aqueous, acidic solution for forming a rare earth element containing coating on the surface of a metal, said solution including effective quantities of:

- 5 (a) one or more rare earth element containing species, including at least one rare earth element capable of having more than one higher valence state; and
- (b) one or more additives selected from the groups including:
- 10 (i) aqueous metal complexes including at least one peroxy ligand; and
- (ii) metal salts or metal complexes of a conjugate base of an acid in which the metals are selected from Transition Elements and Group IVA elements of the Periodic Table.

The invention also provides a process for forming a coating on the surface of a metal, in which the metal surface is contacted with an aqueous, acidic solution including effective quantities of:

- 15 (a) one or more rare earth element containing species, including at least one rare earth element capable of having more than one higher valence state; and
- (b) one or more additives selected from the groups including:
- 20 (i) aqueous metal complexes including at least one peroxy ligand; and
- (ii) metal salts or metal complexes of a conjugate base of an acid in which the metals are selected from the Transition Elements and Group IVA of the Periodic Table.

The invention also extends to a metal surface having deposited thereon a conversion coating formed according to the process of the preceding paragraph.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will now be described with focus on its use for aluminium or aluminium containing alloys. However, a skilled addressee will understand that the invention is not limited to this use.

It may be appropriate for the process of the present invention to be

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preceded by the steps of degreasing and/or cleaning and deoxidising/desmutting the metal surface.

The degreasing step, if present, comprises treatment of the metal surface with any suitable degreasing solution to remove any oils or grease (such as lanoline) 5 or plastic coating present on the metal surface.

The degreasing step, if present, preferably comprises treating the metal surface with a vapour degreasing agent such as tricholoroethane or an aqueous degreasing solution available under the trade name of BRULIN. A degreasing step may be necessary, for example, where the metal has been previously coated with 10 lanoline or other oils or grease or with a plastic coating.

Subsequent to the degreasing step, the metal surface preferably undergoes a cleaning step in order to dissolve contaminants and impurities, such as oxides, from the surface of the metal. Preferably, the cleaning step comprises treatment with an alkaline based solution.

15 The alkaline solution is preferably a "non-etch" solution, that is, one for which the rate of etching of material from the metal surface is low. A suitable alkaline cleaning solution is that commercially available under the trade name RIDOLINE 53.

The treatment with an alkaline cleaning solution is preferably conducted at 20 an elevated temperature, such as up to 80°C, preferably up to 70°C.

Treatment with an alkaline solution often leaves a "smut" on the surface of the metal. As used herein, "smut" is intended to include impurities, oxides and any loosely-bound intermetallic particles which as a result of the alkaline treatment are no longer incorporated into the matrix of the aluminium alloy. It is therefore 25 preferable to treat the metal surface with a "desmutting" or deoxidizing solution in order to remove the smut from the metal surface. Removal of smut is normally effected by treatment with a desmutting (deoxidizing) solution comprising an acidic solution having effective amounts of appropriate additives. Preferably the desmutting solution also dissolves native oxide from the surface of the metal to 30 leave a homogeneously thin oxide on the metal surface. The desmutting solution may be chromate-based. Alternatively, the desmutting solution may be phosphate

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based.

Alternatively again, the desmutting solution may be one which contains rare earth elements such as the solution disclosed in international patent application PCT/AU94/00539 the entire disclosure of which is incorporated herein by reference.

- 5 Treatment with rare earth containing desmutting solutions can further lessen the risk to the environment and health. The rare earth element of the desmutting solution preferably should possess more than one higher valence state. Without wishing to be limited to one particular mechanism of smut removal, it is believed that the multiple valence states of the rare earth element imparts a redox function enabling 10 the rare earth element to oxidise surface impurities and result in their removal as ions into solution. Such rare earth elements are preferably those of the lanthanide series, such as cerium, praseodymium, neodymium, samarium, europium, terbium, erbium and ytterbium. The most preferred rare earth elements are cerium and/or praseodymium and/or a mixture of rare earth elements. Preferably, the rare earth 15 compound is cerium (IV) hydroxide, cerium sulphate, or ammonium cerium (IV) sulphate. The mineral acid is preferably sulphuric acid.

The pH of the rare earth containing desmutting solution is preferably less than 1.

- The rare earth element containing coating solution of the invention 20 contains at least one rare earth element containing species in which the rare earth element has more than one higher valence state. Again, the preferred rare earth elements are those of the lanthanide series. Examples of such rare earth elements are cerium, praseodymium, neodymium, samarium, europium, terbium, erbium and ytterbium ions. The most preferred rare earth element is cerium and/or a mixture of 25 rare earth elements. In the case of a mixture of rare earth elements in the coating solution, typically mischmetal chlorides are used. The typical rare earth elements present in mischmetal chlorides are cerium, praseodymium and lanthanum. Lanthanum has only one higher oxidation state, namely La(III). Accordingly, the mixture of rare earth elements may include other elements in addition to the rare 30 earth elements having more than one higher valence state.

It is particularly preferred that the rare earth element be introduced into

the coating solution in the form of a soluble salt, such as cerium (III) chloride. However other suitable salts include cerium (III) sulphate or cerium (III) nitrate. It is further preferred that the cerium be present in solution as Ce³⁺ cations. Accordingly, when the metal surface is reacted with the coating solution, the 5 resulting pH increase at the metal surface indirectly results in a precipitation of a Ce IV compound on the metal surface. However, the cerium can be present in the solution as Ce⁴⁺, if required.

Throughout the specification, values of concentration or rare earth ions in 10 solution are usually expressed as the equivalent grams of cerium per litre of solution.

The rare earth ion is typically present in the coating solution at a concentration below 50 grams/litre, such as up to 40 g/l. Preferably, the rare earth ion concentration does not exceed 38 g/l. More preferably, the rare earth ion concentration is below 10 g/l, such as up to 7.2 g/l. The lower concentration limit 15 may be 0.038 g/l, such as 0.38 g/l and above. Preferably, the minimum concentration of rare earth ions is 3.8 g/l.

The coating solution may also contain an oxidising agent. The oxidising agent, if present, is preferably a strong oxidant, such as hydrogen peroxide. It may be present in solution in a concentration up to the maximum commercially available 20 concentration (usually around 30 volume %). Usually, however, the H₂O₂ is present at a maximum concentration of 9 volume %. In some embodiments, the H₂O₂ concentration is below 7.5%, preferably below 6%, more preferably below 3%. In other embodiments, particularly those solutions including metal salts or complexes 25 from group (b) (ii) of the additives, the H₂O₂ concentration is preferably above or equal to 0.3%. For those same embodiments, it is further preferred that H₂O₂ concentration is no higher than 1.7%. More preferably, the upper concentration of the H₂O₂ is 0.5 volume %. In further embodiments, the H₂O₂ content is below 1%, preferably below 0.9%, for example about 0.3%. In still further embodiments the H₂O₂ concentration is preferably above 0.03%, such as above 0.15%.

30 The coating solution may also include a surfactant, in an effective amount, in order to lower the surface tension of the solution and facilitate wetting of the metal

surface. The surfactant may be cationic or anionic. Inclusion of a surfactant is beneficial in that by reducing surface tension of the coating solution, it thereby minimises "drag-out" from the solution. "Drag-out" is an excess portion of coating solution which adheres to the metal and is removed from solution with the metal and subsequently lost. Accordingly, there is less waste and costs are minimised by adding surfactant to the coating solution. A surfactant may also help to reduce cracking in the coating. The surfactant may be present in solution at a concentration up to 0.01%, such as 0.005%. A suitable concentration may be up to 0.0025%.

The pH of the coating solution is acidic and in most embodiments the pH is below 4. Preferably, the upper pH limit is 3. More preferably, the pH is 2 or below. While the solution pH may be as low as 0.5, at such low pH values the metal surface is susceptible to etching and coating quality is undermined. The lower limit of solution pH is therefore preferably 1. More preferably, the lower limit of solution pH is 1.2.

The coating solution is used at a solution temperature below the boiling temperature of the solution. The solution temperature is typically below 100°C, such as below 75°C. Preferably, the upper temperature limit is 60°C, such as up to 50°C. In some embodiments, the preferred upper temperature limit is 45°C. The lower temperature limit of the coating solution may be 0°C, although it is preferably ambient temperature.

The metal surface is contacted with the coating solution for a period of time sufficient to give a desired coating thickness. A suitable coating thickness is up to 1µm, such as less than 0.8µm, preferably less than 0.5µm. Preferably, the coating thickness is in the range 0.1 to 0.2µm.

The cleaning and coating steps may be followed by a sealing step. A sealing step can be beneficial under some circumstances. If a sealing step is used, preferably the coated metal surface is rinsed prior to and after the sealing process. The rare earth coating may be sealed by treatment with one of a variety of aqueous or non-aqueous inorganic, organic or mixed sealing solutions. The sealing solution forms a surface layer on the rare earth coating and may further enhance the corrosion resistance of the rare earth coating. Preferably the coating is sealed by an

alkali metal silicate solution, such as a potassium silicate solution. An example of a potassium silicate solution which may be used is that commercially available under the trade name "PQ Kasil #2236". Alternatively, the alkali metal sealing solution may be sodium based, such as a mixture of sodium silicate and sodium orthophosphate. The concentration of the alkali metal silicate is preferably below 5 20%, such as below 15%, more preferably 10% or below. The lower concentration limit of the alkali metal silicate may be 0.001%, such as above 0.01%, preferably above 0.05%.

The temperature of the sealing solution may be up to 100°C, such as up 10 to 95°C. Preferably, the solution temperature is 90°C or lower, more preferably below 85°C, such as up to 70°C. The preferred lower limit of the temperature is preferably ambient temperature, such as from 10°C to 30°C.

The coating is treated with the sealing solution for a period of time sufficient to produce the desired degree of sealing. A suitable time period may be 15 up to 30 minutes, such as up to 15 minutes, and preferably is up to 10 minutes. The minimum period of time may be 2 minutes.

The silicate sealing has the effect of providing an external layer on the rare earth element coating.

The coating solution additives selected from groups (b) (i) and (ii) 20 described above can enhance the coating adhesion to and/or rate of coating on the metal surface.

In the case of additives selected from group (b) (i), the preferred additives are aqueous metal-peroxo complexes. More preferably, the group (b) (i) additives are peroxo complexes of transition metal cations (hereinafter referred to as 25 "transition peroxo complexes"). The following description will concentrate on use of transition peroxo complexes, however a skilled addressee will understand that the invention is not limited to this use. It is preferred that the transition metal cations are chosen from Groups IVB, VB, VIB and VIIIB of the Periodic Table. The peroxo complex may be added as a preformed complex and/or formed *in situ* by a suitable 30 chemical process. Typical additives include peroxo titanium complexes, such as salts of the hydrated $[TiO_2]^{2+}$ cation, peroxovanadium species, such as $[VO(O_2)_2]$.

$[\text{VO(O}_2)]^+$ or $[\text{V(O}_2)_4]^{3-}$, peroxy-niobium or -tantalum complexes, such as $[\text{M(O}_2)_4]^{3-}$ ($\text{M}=\text{Nb}, \text{Ta}$), peroxy-molybdenum or -tungsten species, such as $\text{MoO(O}_2)_2$ or $[\text{M(O}_2)_4]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) or peroxy manganese complexes, such as $[\text{Mn(O}_2)_4]^{4-}$, $[\text{MnO(O}_2)_3]^{n-}$ ($n=3,4$), etc or mixtures thereof.

5 Other group (b) (i) additives may include other ligands in addition to the peroxy ligands. Examples of such additives are complexes of the general formula $[\text{M(O}_2)_2(\text{O}_2)(\text{L})]$ where M may be Cr^{VI}, Mo^{VI} or W^{VI} and L may be an organic ligand. Typical organic ligands are diethylene triamine (det), 2,2,2-triethylenetetraamine (tet) and 2,3,2-triethylenetetraamine (2,3,2-tet). Another group (b) (i) additive including 10 an organic ligand in addition to a peroxy ligand is $\text{Zr(O)(O}_2)(2,3,2\text{-tet})$.

The transition peroxy complexes are present in the coating solution in an effective quantity and may be present at a concentration of up to 500ppm. Preferably, however, the maximum concentration of transition peroxy complexes is 250 ppm. More preferably, the maximum concentration is 180 ppm. Preferably, 15 however, there is more than 10ppm of the transition peroxy complex in the solution.

Alternatively, or in addition to, a transition peroxy complex, the coating solution may include a metal salt or metal complex of an acid which is dissolved in solution or formed in situ and selected from group (b) (ii) defined previously. A requirement of the metal salt or metal complex is that it includes a metal ion selected 20 from the Transition Elements or Group IVA elements of the Periodic Table. The salt or complex may include a transition metal or Group IVA ion and one or more ions derived from various organic or inorganic acids. The organic or inorganic acid may be chosen from acids including hydrochloric acid, carboxylic acids such as acetic or 25 benzoic acid, nitric acid, phosphoric acid, hydrofluoric acid, sulphuric acid, sulphurous acid, sulphamic acid, alkyl- or arylsulphonic acids, alkyl- or arylphosphonic acids, dicarboxylic acids, such as oxalic, citric or malonic acid, etc or mixtures thereof. Typical transition metal ions are silver, manganese, copper, zinc, ruthenium and iron cations. A typical Group IVA metal ion is tin ion.

The preferred amount of the metal complex or salt added to the coating 30 solution varies according to the nature of the metal in the complex or salt. In the following discussion, the concentrations given are those of the chloride salt of the

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transition metal. However, it is to be understood that equivalent concentrations of other metal complexes or salts are within the scope of the invention.

Typically, no more than 2000ppm of the transition metal chloride is used, although in some cases the concentration can be higher. Preferably, no less than 5 10ppm of the transition metal chloride is present in solution. For salts of zinc and manganese, in most cases, relatively high concentrations are preferred. Preferably zinc is present in solution at a concentration of 2000ppm or higher. Preferably, manganese is present at a concentration of up to 1500ppm.

The preferred maximum concentration for copper containing salt is 10 100ppm. The preferred lower concentration for copper containing salt is 50ppm.

For an iron containing salt, the optimum concentration is around 50ppm.

15 The addition of a peroxy complex or a metal complex or salt individually assists in improving coating time and/or adherence of the coating. However, a further improvement in either or both of these parameters can occur if the peroxy complex and metal complex or salt are added to the coating solution in combination. There is accordingly a synergistic effect in adding both types of additives to the coating solution together. There can also be an additional improvement when more than one additive from either or both groups is added to the coating solution.

20

The following Examples illustrate, in detail, embodiments of the invention.

In the Examples, the term "N/A", "SN/A" and "A" mean "non-adherent", "slightly non-adherent" and "adherent", respectively, as determined by a simple tape test. The tape test involves application of adhesive tape to the coated surface, then pulling the 25 tape off to ascertain whether the coating adheres to the metal surface. A non-adherent conversion coating is removed by the tape, whereas for a slightly non-adherent coating only loose material on the surface of the conversion coating is removed by the tape leaving an apparently intact coating behind. For adherent coatings, no coating was removed.

30 The term "N/C" in the Examples means no coating was deposited during the time specified.

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EXAMPLES 1 to 39 AND COMPARATIVE EXAMPLES 1 to 3

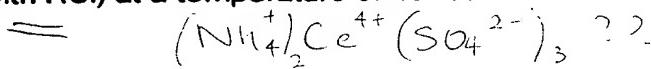
Prior to treatment with the coating solutions described in the following Examples, each metal was pretreated in the following manner:

(a) Treated with an aqueous degreaser (Brulin 815 GD) at 60°C for 10 minutes;

(b) Cleaned with alkaline cleaner (Parker and Amchem, Ridoline 53) at 70°C for 4 minutes; and

(c) Deoxidised in a rare earth containing deoxidising/desmutting solution having a cerium concentration of 0.05 molar, added as ammonium ceric sulphate and a concentration of H₂SO₄ of 0.5 molar at 35°C for 10 minutes.

In each case, the test conversion coating solution contained 13.2 g/l of CeCl₃.7H₂O, 1% of a 30wt% H₂O₂ solution (giving 0.3wt%), and a pH of 2.0 (adjusted, if necessary, with HCl) at a temperature of 45°C.

Comparative Examples 1 to 3

Treatment of particular types of metal alloys, for example 3000, 5000 and 6000 series aluminium alloys, with the test rare earth containing coating solution without the additives of the present invention may yield less than satisfactory results as shown in Table A. Those alloys can be slow to coat and there can be little or no deposition of the rare earth coating within a reasonable time. Furthermore, the adherence of such coatings can be variable.

TABLE A: Coating Characteristics of Test Conversion Coating Solution

25	Comparative Example	Alloy	Coating Time (mins.)	Coating Characteristics
1		3004	18	N/A
2		5005	>60	N/A
30	3	6061	18	S/N/A

$$[(C_1)] = 0.1063 \times 35 \times 10^{-3} = 3.77 \text{ g/l}$$

$$\text{molar}(CeCl_3 \cdot 7H_2O) = 13.2 \times 3(35 \times 10^{-3}) = 4.62 \text{ g/l}$$

$$\approx 37.2 \text{ g/l}$$

$$0.0354 \text{ g/l} \times 37.2 \text{ g/l} = 1.31 \text{ g/l}$$

$$1.10 \text{ g/l}$$

Examples 1 to 6**Table I: Coating Times (minutes) and Characteristics vs Concentration of Mo-peroxo complex.**

5

	Example	Alloy	10ppm	45ppm	90ppm	115ppm	160ppm	160ppm
			pH=2	pH=2	pH=2	pH=2	pH=2.2	pH=1.8
	1	3004	35N/C	18N/A	10N/A	16.5SN/A	12SN/A	18SN/A
10	2	5005	35N/C	35N/A	35N/A	35N/C	20N/C	35N/C
	3	6061	19A	10A	10SN/A	13SN/A	12SN/A	15SN/A

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Table II: Coating Times and Characteristics vs Concentration of Ti-peroxo complex.

15

	Example	Alloy	10ppm	20ppm	50ppm	70ppm	180ppm
			pH=2	pH=2	pH=2	pH=2	pH=1.6
	4	3004	35N/C	15N/A	18SN/A	30N/A	20N/A
20	5	5005	35N/C	30N/A	18N/A	30N/C	20N/C
	6	6061	19 N/A	15 N/A	18 A	30N/A	20 N/C

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As is evident from the data presented in Tables I and II, addition of an appropriate amount of a transition metal-peroxo complex to the rare earth containing coating solution can effect deposition of a conversion coating and/or decrease the time taken to deposit the conversion coating and/or improve the adherence of the conversion coating.

The effect of a particular concentration of a metal-peroxo complex varies for different alloys. However, for each Example, there is an optimum concentration of metal-peroxo complex above which the benefits of the invention decrease. For 3004 aluminium alloy (Examples 1 and 4) addition of more than 10ppm molybdenum

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peroxy complex or titanium peroxy complex resulted in a coating being deposited, whereas addition of more than 90ppm Mo peroxy complex or more than of between 10 and 50ppm Ti peroxy complex resulted in improved adhesion of the coating. Coating time for 3004 alloy was minimised at around 90ppm Mo-peroxy complex.

- 5 Under the particular conditions of Examples 1 and 4, optimum concentrations of Mo-peroxy and Ti-peroxy complexes in terms of coating time and adhesion were around 115 to 160ppm and 50ppm, respectively.

For 5005 aluminium alloy, optimum adhesion and coating time occurred above 10ppm of Mo-peroxy complex and Ti-peroxy complex (Examples 2 and 5). Above 10 90ppm Mo-peroxy complex and 50ppm Ti-peroxy complex, the benefits of the invention decreased.

Best results were obtained for 6061 aluminium alloy, in Examples 3 and 6. Coatings were deposited at concentrations of the two complexes less than 10ppm. Optimum adhesion and coating time were obtained at around 45ppm Mo-peroxy 15 complex and 20 to 50ppm Ti-peroxy complex, with the benefits of the invention decreasing at higher respective concentrations.

Examples 7 to 2720 **Table III: Transition Metal Additions - Coating Time (Mins.) and Characteristics.**

Example	Concentration of Transition Metal(ppm)	Al Alloy	(a)Zn pH=2.2	(b)Mn pH=2.2	(c)Cu pH=2.2	(d)Fe pH=2.2
25 7	10	3004	18N/A	18N/A	7N/A	14N/A
8	10	5005	25N/C	22N/C	16N/A	20N/A
9	10	6061	18N/A	18N/A	7N/A	16N/A

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			pH=2.3	pH=2.3	pH=2.3	pH=2.3
10	50		3004	13N/A	17N/A	6N/A
11	50		5005	30N/A	30N/C	6N/A
12	50		6061	13N/A	17N/A	6SN/A
5						
				pH=2.2	pH=2.2	pH=2.3
13	100		3004	14N/A	20N/A	3A
14	100		5005	18N/A	20N/C	3SN/A
15	100		6061	14SN/A	20N/A	3A
10						
				pH=2.3	pH=2.4	pH=2.4
16	500		3004	9N/A	10N/A	2*
17	500		5005	20N/A	20N/A	2*
18	500		6061	12N/A	14N/A	2*
15						
				pH=2	pH=2	
19	1000		3004	18N/A	16N/A	
20	1000		5005	25N/A	25N/C	
21	1000		6061	18N/A	16SNA	
20						
				pH=1.9	pH=2	
22	1500		3004	16N/A	8N/A	
23	1500		5005	30N/C	22N/A	
24	1500		6061	16N/A	8N/A	
25						
				pH=2	pH=2	
25	2000		3004	12N/A	10N/A	2000 pp~
26	2000		5005	18N/A	25N/A	= <u>2.000 g / ml.</u>
27	2000		6061	12N/A	10N/A	1,000,000 g / liter
30						

* - coating was black, indicating deposition of Cu.

$$\begin{aligned}
 & 2.000 \text{ pp} \sim \\
 & = \frac{2.000 \text{ g}}{1,000,000 \text{ g / liter}} \\
 & \approx 0.002 \text{ g / liter} \\
 & \text{MW(Zn)} = 65 \\
 & 0.002 \text{ g / liter} = \frac{0.002 \text{ mol}}{65} \\
 & = 3 \times 10^{-5} \text{ mol}
 \end{aligned}$$

Table III lists coating times (minutes) and coating characteristics of coatings deposited from solutions containing particular concentrations of four transition metal salts. The transition metals Zn, Mn, Cu and Fe were added to the coating solutions as their respective chlorides, i.e. as $ZnCl_2$, $MnCl_2 \cdot 4H_2O$,
5 $CuCl_2 \cdot 2H_2O$ and $FeCl_2 \cdot 4H_2O$.

As is evident from Table III, addition of increasing amounts of the metal salts to the rare earth containing coating solution results, generally, in a decrease in coating time for all alloys to an optimum concentration, after which in most cases, the benefits of the invention begin to decrease.

10 For addition of Zn, (Examples 7(a) to 27(a)), optimum results in terms of coating time and adherence were obtained at concentrations above 10 to 50ppm, particularly around 100-500ppm and again at higher concentrations around 2000ppm and greater for all alloys.

15 For addition of Mn (Examples 7(b) to 26(b)), the optimum Mn concentration for 3004 alloy occurred above 10ppm, particularly above 500ppm, more particularly around 1500ppm. Whereas for 5005 alloy, the maximum benefit in terms of coating time occurred above 100ppm, particularly around 500ppm. For 6061 alloy, the optimum concentration of Mn was above 500ppm, particularly about 1000ppm in terms of adhesion and above 1000ppm, particularly about 1500ppm in terms of
20 coating time.

Relatively lower concentrations of Cu in the coating solution were effective in improving coating time. For each alloy, improvement in coating time was evident at concentration less than 10ppm. Optimum results were obtained above 50ppm, particularly at around 100ppm. At higher concentrations (particularly around
25 500ppm and greater), the coating quality decreased.

Lower concentrations of Fe in the coating solution were also effective in improving coating time. Concentrations lower than 10ppm were sufficient to achieve the benefit of the invention. Optimum conditions were obtained above 10ppm for each alloy, particularly around 50ppm to 100ppm. At higher concentrations (around
30 500ppm or higher), no coating was deposited.

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Examples 28 to 30**Table IV: Method of Addition of Additives**

5	Example	Alloy	(a)Method 1	(b)Method 2	(c)Combination
					pH=1.9
28		3004	13N/A	12N/A	9A
29		5005	13N/C	20N/C	9A
30		6061	13N/A	12N/C	9A

10

Further improvements in coating times and coating adherence occurs when both a metal peroxy complex of group (b) (i) and a metal salt or complex of group (b) (ii) are added in combination to the coating solution. Table IV demonstrates the synergistic effect of adding both types of additive together to the coating solution.

In Method 1, each alloy was first immersed in a solution having a pH of 2, and 10ppm of Cu (as chloride) for 5 minutes, then immersed in the rare earth ion containing solutions (as described in the preamble to the Examples) further containing 70ppm Ti-peroxy complexes and having a pH of 1.8.

In Method 2, the order of treatment of each alloy was reversed and the alloys were immersed in a solution having 70ppm Ti-peroxy complex and a pH of 2, then subsequently immersed in the rare earth ion containing solution further containing 10ppm Cu (as chloride). In each Example, the combination of the additives of solutions in Methods 1 and 2 produced a much more adherent coating on each alloy in a lower period of time, than the consecutive independent use of each additive.

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Examples 31 to 36**Table V: Transition Metal Salt Additions - Coating Time (Mins.) and Characteristics**

Example	Alloy	<u>Mo-peroxo complex (90ppm)</u>				<u>(100ppm)</u>
		(a) Zn (50ppm)	(b) Mn (50ppm)	(c) Cu (10ppm)	(d) Fe (50ppm)	(e) Cu (10ppm)
		pH=2	pH=2	pH=2	pH=2	pH=2
31	3004	15SN/A	14SN/A	8A	13SN/A	10A
32	5005	22N/A	22N/A	8N/A	20N/A	10N/A
33	6061	15A	14A	8A	13SN/A	10A

<u>Ti-peroxo complex (70ppm)</u>				
	pH=2	pH=2	pH=1.9	pH=2.3
34	20N/C	24N/A	9A	22SN/A
35	20N/C	24N/C	9A	22N/C
36	20N/C	24N/C	9A	22SN/A

Examples 31 to 36 further illustrate the advantage in adding both group (b) (i) and group (b) (ii) additives to the coating solution. Comparison of each of Examples 31, (a,b,c,d,e), 32(a,b,c,d,e), 33(a,b,c,d,e), 34(a,b,c,d), 35(a,b,c,d) and 36(a,b,c,d) with a corresponding, previously discussed Example and having the same concentration of metal-peroxo complex or metal salt, illustrates in most cases, the further improvement in coating time and coating adhesion that both additives in combination provide. A particularly preferred coating solution is one containing 70ppm Ti-peroxo complex and 10ppm Cu (Examples 34(c), 35(c) and 36(c)) which, provides an adherent coating on all three alloys in a short period of time (around 9 minutes).

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Examples 37 to 39**Table VI: Mixture of Additives**

5	Example	Alloy	Mo+Mn+Cu pH = 2.0	90ppm	50ppm	10ppm
				Mo-peroxo Complex	Mn-Salt	Cu Salt
	37	3004	5SNA	18N/A	17N/A	7N/A
10	38	5005	5SNA	35N/C	30N/C	16N/A
	39	6061	5A	10A	17N/A	7N/A

Further improvements in coating time and/or coating adherence are possible by adding more than one additive from group (b) (ii) metal salts. As Table VI demonstrates, addition of 90ppm Mo-peroxo complex, 50ppm Mn salt (as chloride) and 10ppm Cu salt (as chloride) results in faster coating times and improved adhesion of coating than for separate addition of each additive to the coating solution.

20 EXAMPLE 40 and COMPARATIVE EXAMPLE 4

For each of Example 40 and Comparative Example 4, a piece of Al 5005 alloy was pretreated by abrasion of the surface, then treated with a coating solution.

Table VIII: Addition of Ruthenium Salt

25

	Example	Ru Salt (g/l)	Coating (mins)
	40	4.5×10^{-4}	60
30	4 (comp)	0	>60

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The coating solution included 10 g/l $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 1% H_2O_2 . The pH of the coating solution was adjusted to 2.0 with HCl addition and the coating process was conducted at a temperature of 45°C. For Example 40, the coating solution additionally included 4.5×10^{-4} g/l RuCl_3 . *not a REE*

5 The results show that the presence of ruthenium in the coating solution results in the deposition of a coating within 60 minutes. Comparative Example 4 indicates that treatment with the same solution with ruthenium omitted results in no coating being deposited after 60 minutes.

10 Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the compositions and/or steps previously described without departing from the spirit or ambit of the invention.

$$\text{molar RuCl}_3 = 101 + 3(35.5) \\ = 207.5$$

$$15 \quad 4 \times 10^{-4} \text{ g/l} = \frac{4.5 \times 10^{-4}}{207.5} = 2.1 \times 10^{-6} \text{ mol/l}$$

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CLAIMS

1. An aqueous, acidic solution for forming a rare earth element containing coating on the surface of a metal, said solution including effective quantities of:
 - 5 (a) one or more rare earth element containing species including at least one rare earth element capable of having more than one higher valence state, as herein defined; and
 - (b) one or more additives selected from the groups including:
 - (i) aqueous metal complexes including at least one peroxy ligand; and
 - 10 (ii) metal salts or aqueous metal complexes of a conjugate base of an acid in which the metals are selected from Transition Elements and Group IVA elements of the Periodic Table as herein defined.
 2. The aqueous, acidic solution of claim 1, wherein the Transition Elements of group (b) (ii) include silver, manganese, copper, zinc, ruthenium and iron.
 - 15 3. The aqueous, acidic solution of claim 1 or claim 2, wherein the Group IVA element of group (b) (ii) is tin.
 4. The aqueous, acidic solution of any preceding claim, wherein the conjugate base of an acid of group (b) (ii) is derived from one or more of the following acids:
 - hydrochloric acid, carboxylic acid, nitric acid, phosphoric acid, hydrofluoric acid, sulphuric acid, sulphurous acid, sulphamic acid, alkyl or arylsulphonic acids, alkyl or aryl phosphonic acids, dicarboxylic acids and mixtures thereof.
 - 20 5. The aqueous, acidic solution of any preceding claim, wherein the one or more rare earth element containing species of group (a) contain cerium and/or a mixture of rare earth elements.
 6. The aqueous, acidic solution of any preceding claim wherein the rare earth element containing species of group (a) is provided by an aqueous solution of one or more of the compounds: cerium (III) chloride, cerium (III) sulphate and cerium (III) nitrate.
 - 25 7. The aqueous, acidic solution of any preceding claim wherein the rare earth element containing species comprises cerium containing ions at a concentration of cerium of up to 10 grams/litre.
 - 30

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8. The aqueous, acidic solution of claim 7, wherein the concentration of cerium is between 3.8 and 7.2 grams/litre.
9. The aqueous, acidic solution of any one of claims 1 to 8, wherein the aqueous metal complex of group (b)(i) is formed in situ in said solution.
10. The aqueous, acidic solution of any one of claims 1 to 8, wherein the aqueous metal complex of group (b)(i) is formed prior to its addition to said solution.
11. The aqueous, acidic solution of any preceding claim, wherein the aqueous metal complexes of group (b) (i) are peroxy complexes of Transition Metal cations.
12. The aqueous, acidic solution of any preceding claim, wherein the aqueous metal complexes of group (b) (i) are peroxy complexes of metals selected from Groups IVB, VB, VIB and VIIIB of the Periodic Table as herein defined.
13. The aqueous, acidic solution of any preceding claim, wherein the aqueous metal complexes of group (b) (i) are selected from the group comprising:
peroxy titanium complexes, peroxy vanadium complexes, peroxy niobium complexes, peroxy tantalum complexes, peroxy molybdenum complexes, peroxy tungsten complexes, peroxy manganese complexes, peroxy zirconium complexes and mixtures thereof.
14. The aqueous, acidic solution of any preceding claim, further including an oxidising agent.
15. The aqueous, acidic solution of claim 14, wherein the oxidising agent is hydrogen peroxide.
16. The aqueous, acidic solution of any preceding claim, wherein the concentration of the aqueous metal complex of group (b) (i) is between 10 and 500 ppm.
17. The aqueous, acidic solution of any preceding claim, wherein the concentration of the aqueous metal complex of group (b) (i) is between 10 and 250 ppm.
18. The aqueous, acidic solution of any preceding claim, wherein the concentration of the aqueous metal complex of group (b) (i) is between 10 and 180 ppm.
19. The aqueous, acidic solution of any preceding claim, wherein the

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- concentration of the metal complex of group (b) (ii) is between 10 and 2000 ppm.
20. The aqueous, acidic solution of any one of claims 14 to 19 wherein the concentration of the oxidising agent is between 0.3 and 1.7 volume %.
21. The aqueous, acidic solution of any one of claims 14 to 20 wherein the concentration of the oxidising agent is between 0.3 and 0.5 volume %.
- 5 22. The aqueous, acidic solution of any preceding claim, wherein the pH of the aqueous acidic solution is less than 4.
23. The aqueous, acidic solution of any preceding claim, wherein the pH of the aqueous acidic solution is between 1 and 2.5.
- 10 24. The aqueous, acidic solution of any preceding claim, wherein the temperature of the aqueous acidic solution is between ambient and 60°C.
25. The aqueous, acidic solution of any preceding claim, including one or more additives selected from each of groups (b) (i) and (b) (ii).
- 15 26. A process for forming a coating on the surface of a metal, including the step of contacting the metal surface with an aqueous acidic solution including effective quantities of:
- (a) one or more rare earth element containing species including at least one rare earth element capable of having more than one higher valence state, as herein defined; and
- 20 (b) one or more additives selected from the groups including:
- (i) aqueous metal complexes including at least one peroxy ligand; and
- (ii) metal salts or aqueous metal complexes of a conjugate base of an acid in which the metals are selected from Transition Elements and Group IVA elements of the Periodic Table as herein defined.
- 25 27. The process of claim 26, wherein the Transition Elements of group (b) (ii) include silver, manganese, copper, ruthenium, zinc and iron.
28. The process of claim 26 or 27, wherein the Group IVA element of group (b) (ii) is tin.
29. The process of any one of claims 26 to 28, wherein the conjugate base of an acid of group (b) (ii) is derived from one or more of the following acids:
- 30 hydrochloric acid, carboxylic acid, nitric acid, phosphoric acid, hydrofluoric

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- acid, sulphuric acid, sulphurous acid, sulphamic acid, alkyl or arylsulphonic acids, alkyl or aryl phosphonic acids, dicarboxylic acids and mixtures thereof.
30. The process of any one of claims 26 to 29, wherein the one or more rare earth element containing species of group (a) contain cerium and/or a mixture of rare earth elements.
31. The process of any one of claims 26 to 30, wherein the rare earth element containing species of group (a) is provided by an aqueous solution of one or more of the compounds: cerium (III) chloride, cerium (IV) sulphate and cerium (III) nitrate.
32. The process of any one of claims 26 to 31, wherein the rare earth element containing species comprises cerium containing ions at a concentration of cerium of up to 10 grams/litre.
- 10 33. The process of claim 32, wherein the concentration of cerium is between 3.8 and 7.2 grams/litre.
34. The process of any one of claims 26 to 33, wherein the aqueous metal complex of group (b)(i) is formed in situ in said solution.
- 15 35. The process of any one of claims 26 to 33, wherein the aqueous metal complex of group (b)(i) is formed prior to its addition to said solution.
36. The process of any one of claims 26 to 35, wherein the aqueous metal complexes of group (b) (i) are peroxy complexes of Transition Metal cations.
- 20 37. The process of any one of claims 26 to 36, wherein the aqueous metal complexes of group (b) (i) are peroxy complexes of metals selected from Groups IVB, VB, VIB and VIIIB of the Periodic Table as herein defined.
38. The process of any one of claims 26 to 37, wherein the aqueous metal complexes of group (b) (i) are selected from the group comprising:
- 25 peroxy titanium complexes, peroxy vanadium complexes, peroxy niobium complexes, peroxy tantalum complexes, peroxy molybdenum complexes, peroxy tungsten complexes, peroxy manganese complexes, peroxy zirconium complexes and mixtures thereof.
39. The process of any one of claims 26 to 38, further including an oxidising agent.
- 30 40. The process of claim 39, wherein the oxidising agent is hydrogen peroxide.
41. The process of any one of claims 26 to 40, wherein the concentration of the

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- aqueous metal complex of group (b) (i) is between 10 and 500 ppm.
42. The process of any one of claims 26 to 41, wherein the concentration of the aqueous metal complex of group (b) (i) is between 10 and 250 ppm.
43. The process of any one of claims 26 to 42, wherein the concentration of the aqueous metal complex of group (b) (i) is between 10 and 180 ppm.
44. The process of any preceding claim, wherein the concentration of the metal complex of group (b) (ii) is between 10 and 2000 ppm.
45. The process of any one of claims 39 to 44, wherein the concentration of the oxidising agent is between 0.3 and 1.7 volume %.
46. The process of any one of claims 39 to 45, wherein the concentration of the oxidising agent is between 0.3 and 0.5 volume %.
47. The process of any one of claims 26 to 46, wherein the pH of the aqueous acidic solution is less than 4.
48. The process of any one of claims 26 to 47, wherein the pH of the aqueous acidic solution is between 1 and 2.5.
49. The process of any one of claims 26 to 48, wherein the temperature of the aqueous acidic solution is between ambient and 60°C.
50. The process of any one of claims 26 to 49, wherein the aqueous acidic solution includes one or more additives selected from each of groups (b) (i) and (b) (ii).
51. The process of any one of claims 26 to 50, wherein the step of contacting the metal surface comprises contacting an aluminium or an aluminium containing alloy surface with said aqueous acidic solution.
52. The process of claim 51, wherein the aluminium containing alloy is selected from 3000, 5000 and 6000 series aluminium alloys.
53. The process of any preceding claim, wherein the step of contacting the metal surface with said aqueous acidic solution is preceded by the steps of degreasing and/or alkaline cleaning and desmutting the metal surface.
54. The process of claim 53, wherein the step of desmutting comprises treating the metal surface with an acidic, rare earth containing desmutting solution.
55. The process of claim 54, wherein the acidic, rare earth containing desmutting

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solution includes cerium and/or praseodymium and/or a mixture of rare earth elements, and H₂SO₄.

56. The process of claim 54 or claim 55, wherein the acidic, rare earth containing desmutting solution has a pH of less than 1.

5 57. A metal surface having thereon a rare earth element containing coating formed by a process according to any one of claims 26 to 56.

58. An aqueous, acidic solution for forming a rare earth element containing coating on the surface of a metal, substantially as herein described with reference to any one of Examples 1 to 40.

10 59. A process for forming a coating on the surface of a metal including the step of contacting the metal surface with an aqueous acidic solution, substantially as herein described with reference to any one of Examples 1 to 40.

60. A metal surface having thereon a rare earth element containing coating, substantially as herein described with reference to any one of Examples 1 to 40.

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AMENDED CLAIMS

[received by the International Bureau on 27 March 1995 (27.03.95);
original claims 1 and 26 amended; remaining claims unchanged (2 pages)]

1. An aqueous, acidic solution for forming a rare earth element containing coating on the surface of a metal, said solution being chromium free and including effective quantities of:
 - 5 (a) one or more rare earth element containing species including at least one rare earth element capable of having more than one higher valence state, as herein defined; and
 - (b) one or more additives selected from the groups including:
 - (i) aqueous metal complexes including at least one peroxy ligand; and
 - 10 (ii) metal salts or aqueous metal complexes of a conjugate base of an acid in which the metals are selected from Transition Elements, other than chromium, and Group IVA elements of the Periodic Table as herein defined.
 2. The aqueous, acidic solution of claim 1, wherein the Transition Elements of group (b) (ii) include silver, manganese, copper, zinc, ruthenium and iron.
 - 15 3. The aqueous, acidic solution of claim 1 or claim 2, wherein the Group IVA element of group (b) (ii) is tin.
 4. The aqueous, acidic solution of any preceding claim, wherein the conjugate base of an acid of group (b) (ii) is derived from one or more of the following acids:
 - 20 hydrochloric acid, carboxylic acid, nitric acid, phosphoric acid, hydrofluoric acid, sulphuric acid, sulphurous acid, sulphamic acid, alkyl or arylsulphonic acids, alkyl or aryl phosphonic acids, dicarboxylic acids and mixtures thereof.
 5. The aqueous, acidic solution of any preceding claim, wherein the one or more rare earth element containing species of group (a) contain cerium and/or a mixture of rare earth elements.
 - 25 6. The aqueous, acidic solution of any preceding claim wherein the rare earth element containing species of group (a) is provided by an aqueous solution of one or more of the compounds: cerium (III) chloride, cerium (III) sulphate and cerium (III) nitrate.
 - 30 7. The aqueous, acidic solution of any preceding claim wherein the rare earth element containing species comprises cerium containing ions at a concentration of cerium of up to 10 grams/litr .

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concentration of the metal complex of group (b) (ii) is between 10 and 2000 ppm.

20. The aqueous, acidic solution of any one of claims 14 to 19 wherein the concentration of the oxidising agent is between 0.3 and 1.7 volume %.

21. The aqueous, acidic solution of any one of claims 14 to 20 wherein the 5 concentration of the oxidising agent is between 0.3 and 0.5 volume %.

22. The aqueous, acidic solution of any preceding claim, wherein the pH of the aqueous acidic solution is less than 4.

23. The aqueous, acidic solution of any preceding claim, wherein the pH of the aqueous acidic solution is between 1 and 2.5.

10 24. The aqueous, acidic solution of any preceding claim, wherein the temperature of the aqueous acidic solution is between ambient and 60°C.

25. The aqueous, acidic solution of any preceding claim, including one or more additives selected from each of groups (b) (i) and (b) (ii).

26. A process for forming a coating on the surface of a metal, including the 15 step of contacting the metal surface with an aqueous acidic solution being chromium free and including effective quantities of:

(a) one or more rare earth element containing species including at least one rare earth element capable of having more than one higher valence state, as herein defined; and

20 (b) one or more additives selected from the groups including:

(i) aqueous metal complexes including at least one peroxy ligand; and

(ii) metal salts or aqueous metal complexes of a conjugate base of an acid in which the metals are selected from Transition Elements, other than chromium, and Group IVA elements of the Periodic Table as herein defined.

25 27. The process of claim 26, wherein the Transition Elements of group (b) (ii) include silver, manganese, copper, ruthenium, zinc and iron.

28. The process of claim 26 or 27, wherein the Group IVA element of group (b) (ii) is tin.

29. The process of any one of claims 26 to 28, wherein the conjugate base of 30 an acid of group (b) (ii) is derived from one or more of the following acids:

hydrochloric acid, carboxylic acid, nitric acid, phosphoric acid, hydrofluoric

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STATEMENT UNDER ARTICLE 19

Claims 1 and 26 have been amended to specify that the aqueous acidic solution is chromium-free and that the Transition Elements of group (b) (ii) additives are other than chromium. Support for the explicit exclusion of chromium can be found at pages 1 and 2 of the specification. The problems of prior art conversion coating processes using chromate (ie. chromium containing) solutions are discussed. The specification goes on to state that an object of the invention is to provide an alternative conversion coating solution and process which overcome or alleviate at least one of those problems. Thus, we submit that there is a clear implication that the coating solutions of the present invention do not include chromium.

The amendments assist in distinguishing the claims from the prior art located in the International Search Report, in particular US 4,349,392 to Huvar.

INTERNATIONAL SEARCH REPORT

International Application N PCT/AU 95/00745
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A. CLASSIFICATION OF SUBJECT MATTERInt Cl⁶: C23C 22/16 22/18 22/53 22/56 C23F 7/02 7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : C23C 22/16 22/18 22/53 22/56 C23F 7/02 7/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JAPIO : rare earth: cerium: erbium: etc. lanthanide: group: IVA: tin: etc.

WPAT : rare earth: cerium: erbium: etc. lanthanide: group IVA: tin: etc.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4349392 A (HUVAR) 14 September 1982 The abstract, examples and claim 1	1-2, 4-27, 29-37 & 39-60 3, 28 & 38
Y		
Y	EP 0603921 A1 (METALLGESELLSCHAFT AG) 29 June 1994 Column 2 line 45 - column 3 line 14	1-60
Y	AU 14858/88 A (COMMONWEALTH OF AUSTRALIA) 7 September 1988 Page 6 lines 12-23 and claims	1-60

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

22 January 1996

Date of mailing of the international search report

02 FEB 1996

Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
 PO BOX 200
 WODEN ACT 2606
 AUSTRALIA Facsimile No.: (06) 285 3929

Authorized officer
SUDATH KUMARASINGHE
 Telephone No.: (06) 283 2269

INTERNATIONAL SEARCH REPORT**Information on patent family members**

International Application No.

PCT/AU 95/00745

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	603921	CA US	2111165 5383982	DE	4243214	JP	6228766
US	4349392	AU HK CA JP ES NL	82634/82 855/86 1228000 57181379 8401148 185856	GB BR IT ES MX SE	2097024 8202218 1147842 511465 160353 8202372	BE IT DE JP FR SG	892885 8248225 3213384 3010714 2504156 676/86
AU	14858/88	CA ZA	1292155 8801481	WO JP	8806639 2502655	EP NZ	347420 223740
END OF ANNEX							